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PATENT APPLICATION

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43 Date of public disclosure of the application: BOPI "Bulletin" No. 13 of 29 March 1985.	72 Inventor(s): <i>Insan Barin and Roland Pfeiffer.</i>
60 References to other related national documents:	73 Holder(s): 74 Representative(s): <i>Cabinet Armengaud Jeune, Casanova and Lapeudry.</i>

54 Process and apparatus for preparation of a synthesis gas consisting of hydrogen and carbon monoxide by gasification of carbon-containing materials in an iron bath reactor

57 Process and apparatus for preparation of a synthesis gas consisting of hydrogen and carbon monoxide by gasification of carbon-containing materials in an iron bath reactor.

A carbon-containing material 5, especially coal, is gasified in an iron bath reactor 1 in the presence of flux 6 and oxygen 15, 4, 16. The gas is enriched in hydrogen, coming from an electrolysis cell 3 with an elevated water vapor temperature 11, in a cooling vessel 2. The mixer 48 of gas 13 and hydrogen 14 yields a synthesis gas 49 containing 2 mol hydrogen per 1 mol CO. Application: direct production of methanol.

The invention concerns a process and apparatus for preparation of a synthesis gas consisting of hydrogen and carbon monoxide.

One can mention as materials to be employed all carbon-containing materials, like residual heavy crudes, but especially solid carbon-containing materials from peat, through charcoal, lignite, to oils rich in sulfur, with introduction of reaction additives, like slag generators and gasification agents, preferably industrial oxygen and hydrogen.

For example, it is known from Patent Application DE-A-3 137 755 to gasify carbon-containing materials in a reactor containing molten iron, which produces a synthesis gas, consisting of hydrogen and carbon monoxide. However, because of the unfavorable molar ratio of hydrogen to carbon monoxide, this synthesis gas cannot be subsequently used.

The invention therefore seeks to prepare a synthesis gas having a specified stoichiometric composition, and which can therefore be used directly for a subsequent conversion process, by using new technical aspects and economic viewpoints, while obtaining the highest possible yield and avoiding the known inadequate conventional processes.

The problem as posed is solved by subjecting a gas without sulfur, obtained in an iron bath reactor by gasification of carbon-containing materials, especially coal, to enrichment with additional hydrogen, so that, as synthesis gas, it has a molar ratio of 2 mol hydrogen per 1 mol of carbon monoxide.

By using an iron bath reactor as gasifier, a synthesis gas largely devoid of carbon dioxide can be produced very advantageously and in simple and economical fashion. Special desulfuration treatment of the synthesis gas is not necessary and, in comparison with conventional gasification processes, corresponding parts of the installation can be omitted.

By additional hydrogen enrichment, which can advantageously be produced in the process of the invention, constant regulation of the molar ratio in the synthesis gas of 2 mol hydrogen per 1 mol carbon monoxide is permitted or guaranteed, which permits this enriched synthesis gas to be used directly as a raw material for a subsequent conversion process, merely regulating the use parameters.

In a development of the invention, it is prescribed that the synthesis gas having a molar ratio of 2 mol hydrogen per 1 mol carbon monoxide be used as a raw material for methanol synthesis. Thus, starting from coal at an advantageous price, which can have poor caking capacity, as well as fairly high sulfur and ash contents, one obtains a process for methanol

preparation using coal, and one that is even economically advantageous in comparison with conventional processes for preparation of methanol based on natural gas, naphtha or heavy heating oils.

In another development of the invention, it is prescribed to pass the gas produced in the iron bed reactor through a cooling vessel and to then enrich it with additional hydrogen.

The gas produced in the cooling vessel is cooled from about 1400°C to about 150°C, and the heat energy can be advantageously exploited and used to heat other parts of the installation, or to produce the gasification agent. After cooling of the produced gas and dust elimination, it is enriched with additional hydrogen, the amount of which permits a stoichiometric ratio of hydrogen to carbon monoxide to be precisely achieved for subsequent direct synthesis of methanol.

In a development of the process, it is prescribed to produce, by electrolysis at elevated steam temperature, the additional hydrogen intended to enrich the gas produced in the iron bath reactor.

Electrolysis at elevated temperature very advantageously permits an improvement in profitability of water vapor decomposition by reducing the consumption of electrical power at elevated temperatures, owing to the reduction in voltage of the reversible cells and improvement of the conductivity of the electrolyte.

In a special development of the process of the invention, it is prescribed to break down water vapor by operating electrolysis at elevated temperature, preferably under a pressure of 35 bar at a temperature of 800°C, which decomposes the water vapor to hydrogen and oxygen. These operating parameters permit an optimal reduction of electrical power consumption for production of hydrogen and oxygen.

In another development of the invention, it is prescribed to produce the water vapor intended for electrolysis at elevated temperature in the cooling vessel.

In this manner, one can very advantageously retain the enthalpy of the gas produced in the process and use it to produce the water vapor as feed medium and to heat the electrolysis cell.

In another development of the invention, it is prescribed to pass the hydrogen and oxygen produced during hydrolysis at elevated temperature through the cooling vessel. One can then also obtain cooling of the pure gases by using the heat energy that they contain.

In another development of the invention, it is prescribed to partially send the oxygen produced by electrolysis at elevated temperature to the iron bath reactor. The gasification process that occurs in the iron bath reactor is therefore supplied with oxygen, which serves as gasification agent, and which very advantageously comes from the process itself. The excess oxygen produced can be fed to other applications, for example, introduced to a network of oxygen feed lines in the plant.

In another development of the invention, it is prescribed to produce the hydrogen that will be fed to the iron bath reactor in the cooling vessel, advantageously at 3 bar. In this manner, one can produce very advantageously the hydrogen that serves as gasification agent in the cooling vessel at a favorable pressure of 3 bar, using the heat energy of the produced gas and using the hydrogen and oxygen produced in the gaseous state during electrolysis at elevated temperature.

In another development of the invention, the gas produced in the iron bath reactor is partly passed through a stage of conversion of carbon monoxide and a stage of adsorption of carbon dioxide. Thus, at sites where the electrical power is too burdensome or not very profitable for exploitation of an electrolysis cell, one can advantageously resort to another possibility that consists of treating the gas produced in the iron bath reactor, so that the synthesis gas that results has the necessary stoichiometric molar ratio.

For this purpose, additional hydrogen is obtained according to the invention, intended to enrich the gas produced in the iron bath reactor by conversion of carbon monoxide to hydrogen and carbon dioxide. One can therefore very simply accomplish hydrogen enrichment by conversion of carbon monoxide, present in excess in the produced gas.

In a special variant of this variant of the process, it is prescribed to carry out conversion of carbon monoxide by injection of water into the gas coming from the iron bed reactor, which is advantageously at 1400°C. In what is called cooling/conversion, even without catalysts, water/gas equilibrium is produced very rapidly, with formation of hydrogen and carbon dioxide at temperatures greater than about 950°C. Below about 950°C, it is recommended that carbon monoxide conversion be accelerated by surfaces with a catalytic role, consisting, for example, of cobalt and nickel compounds.

By injection of water into the gas produced in the process, one advantageously maintains the enthalpy of the gas so produced in the conversion process to produce water vapor

and to cool the gas so produced to about 570°C, so that the resulting synthesis gas still contains CO₂, but has the necessary stoichiometric ratio of hydrogen to carbon monoxide.

To separate the gaseous CO₂ forming part of the synthesis gas, it is prescribed according to the invention to eliminate the CO₂ from the synthesis gas by absorption with potassium carbonate. Absorption, for example, absorption with hot potassium carbonate in a stage with divided flow, permits extraction of CO₂ from the synthesis gas in very simple and particularly profitable fashion, to arrive at residual contents less than 0.5 vol.%. In the process according to the invention, one can advantageously use the enthalpy of the produced gas to partially heat the desorption column during absorption of CO₂, which reduces the necessary outside energy.

The process of the invention will now be described in greater detail, as a non-limiting example, with reference to the appended drawing, in which Figures 1 and 2 are schematic modular representations of this process, and in relation to the data shown especially in Tables 1 and 2.

As shown in Figure 1, 50 tonnes of coal per hour as solid is continuously fed to an iron bath reactor 1 to produce a gas low in sulfur and consisting essentially of hydrogen and carbon monoxide, through an introduction line 5, and 10 t/h of fluxes or additives are supplied through introduction line 6. In example 1 of the calculation according to Table 1, the fluxes or additives consist of quick lime CaO. One can also use limestone CaCO₃, dolomite CaMg(CO₃)₂ or other substances with a basic slag-generating role as flux. The liberated CO₂, during calcining in the iron bath reactor 1, is completely converted at the elevated operating temperatures of about 1400°C to carbon monoxide, according to the Boudouard reaction with solid carbon.

As gasification agents, oxygen is introduced to the iron bath reactor 1 through gas line 16, as well as water vapor through gas line 12. The slag for sulfur fixation, indicated by CaS in Table 1, and which is obtained during gasification of the carbon-containing materials, is withdrawn from reactor 1 continuously or batchwise in an amount of 16 t/h through a slag output 8.

The gas so produced leaves iron bath reactor 1 at a temperature of about 1400°C through a gas line 7, and from there is fed to a cooling vessel 2 in which it is cooled to about 150°C.

The water vapor in the electrolysis cell 3 at elevated temperature, connected to cooling vessel 2, is broken down to oxygen and hydrogen at 800°C under a pressure 35 bar. The hydrogen goes to cooling vessel 2 through gas line 19, in which, in the same manner as the produced gas, it is cooled to about 150°C. The hydrogen and the produced gas are withdrawn separately from each other from cooling vessel 2. The hydrogen leaves the cooling vessel 2 through gas line 14 and, parallel to it, cooled gas leaves vessel 2 through gas line 13. Lines 13 and 14 discharge into a gas mixer 48, in which the gas obtained in the process and the hydrogen coming from cooling vessel 2 are mixed with each other. The gas obtained in the process is thus enriched according to the invention with hydrogen, so that a synthesis gas is produced having a stoichiometric molar ratio, and which can be used as a raw material, for example, for methanol synthesis. This synthesis gas re-equilibrated in this way can be directly fed through line 49 to this methanol synthesis.

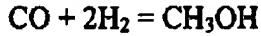
The heat energy of the gas obtained in the process in cooling vessel 2 serves to produce water vapor. On the one hand, water vapor is advantageously prepared as gasification agent for the iron bath reactor 1, and, on the other hand, water vapor intended to feed electrolysis 3 carried out at elevated temperature is produced. Through water line 10, water is fed under a pressure of 3 bar to cooling vessel 2, in which it is converted to vapor fed through gas line 12 to iron bath reactor 1. The water vapor produced by means of heat originating from the process in the cooling vessel serves as a gasification agent of the carbon-containing material. One therefore obtains very advantageously a situation in which the system itself produces the water vapor necessary as gasification agent for the gasification process. It is therefore not necessary to prepare the water vapor outside at other sources. The water under a pressure of 35 bar is introduced through line 9 to cooling vessel 2, in which it is converted to superheated steam that the steam line 11 supplies to feed electrolysis performed at elevated temperature. The use of electrolysis at elevated temperature very advantageously permits a reduction in electrical power consumption, introduced by conductor 20 in electrolysis cell 3. The oxygen produced during electrolysis at elevated temperature in cell 3 is fed via line 18 to cooling vessel 2 and cooled there from 800°C to 150°C. According to the invention, after having given up its heat energy in vessel 2, the oxygen obtained by electrolysis at elevated temperature serves as gasification agent of the carbon-containing material used to prepare the gas by the process of the invention. One therefore very advantageously obtains a situation in which the necessary oxygen is produced and

used in the process itself, and it is not necessary to obtain oxygen from the outside. The oxygen goes from cooling vessel 2 via gas line 15 to an expansion stage 4 and through a gas line 16 to reactor 1, where it serves as gasification agent. The excess oxygen is taken off through a gas line 15 and withdrawn through gas bypass line 17 that enables it to be sent to other uses.

Two examples of application permit a calculation of the material and energy balance for technical or industrial employment of methanol synthesis according to the invention:

Example 1

Preparation of raw materials for industrial employment of methanol synthesis is involved:



in an installation, whose daily production, for example, is 2500 tonnes CH_3OH , with the operating parameters:

$p = 30$ to 50 bar, T : about 350°C , and

ΔH_R (623 K) = -101.59 kJ/mol

$2500 \text{ t CH}_3\text{OH/day} \approx 3255 \text{ kmol CH}_3\text{OH/h}$

The necessary material streams therefore represent:

CO: $3255 \text{ kmol/h} = 904 \text{ mol/s}$

H_2 : $6510 \text{ kmol/h} = 1808 \text{ mol/s}$

These material streams are produced in an iron bath reactor, whose internal volume has a capacity of 100 tonnes of molten iron.

The specific consumption of coal necessary is about 0.5 tonne coal per tonne of molten iron per hour. The cell for electrolysis at elevated temperature, used in the present calculation example, consists of a solid electrolyte that conducts oxygen ions, preferably stabilized zirconium oxide, and semiconducting electrodes by oxidation, preferably formed from lanthanum and cobalt compounds or lanthanum and chromium compounds, containing dopants. The resistivity ρ of the solid electrolyte is $40 \Omega \cdot \text{cm}$ for a reaction temperature of 800°C , the volumetric power or power density is 2000 W/m^2 , the electrode surface represents $149\,900 \text{ m}^2$.

To obtain the necessary molar ratio from methanol synthesis, one must produce, by high temperature electrolysis, 1238 mol of hydrogen per second. To produce this amount of hydrogen, the following thermodynamic reaction conditions are suitable ($p = 35$ bar, $T = 800^\circ\text{C}$):

Energy requirement of the reaction:

$\Delta H_R = 308.3 \text{ MW}$

External energy (electrical power):	$\Delta G_R = 253.6 \text{ MW}$
Entropy (heat):	$T \Delta S_R = 54.2 \text{ MW}$
Heat production by the cell:	45.7 MW
Electrical power consumption:	299.3 MW
Reversible cell voltage, FEM:	1.06 V
Electrolysis voltage:	$\Delta U_{\text{tot}} = 1.25 \text{ V}$
Voltage drop through ohmic resistance of the electrolyte:	$U = 0.19 \text{ V}$

In the present calculation example polarization losses are not taken into account because they are very different or depend on each electrode material. During implementation of the apparatus of the invention, one must, however, account for polarization losses.

As necessary heat for the process, one must provide to the cell:

(54.2 MW = 45.7 MW) = 8.5 MW.

This amount of heat is obtained by superheating the steam used in the process from 800°C to 970°C.

TABLE 1

Line	Medium or agent in mol/s	MW	T, K	P, bar	
5	Coal	50 t/h	-35,5	298	-
6	Flux (CaO)	10 t/h	-31,7	298	-
7	CO : 904, H ₂	570	-31,3	1673	3
8	Slag (CaS)	16 t/h	-42,8	1673	-
9	H ₂ O	1238	-354,0	298	35
10	H ₂ O	29	-8,3	298	3
11	H ₂ O	1238	-255,3	1243	35
12	H ₂ O	29	-6,9	400	3
13	CO : 904, H ₂	570	-94,2	423	3
14	H ₂	1238	4,5	423	35
15	O ₂	619	2,3	423	35
16	O ₂	431	0	298	3
17	O ₂	188	0,7	423	35
18	O ₂	619	15,5	1073	35
19	H ₂	1238	28,5	1073	35
20	Electrical power	299,3 MW	-	-	-

Figure 2 shows a variant for production of synthesis gas for methanol preparation.

Example 2

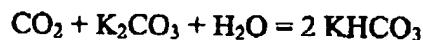
Starting from the same base conditions for methanol synthesis, according to example 2 and Table 2, one introduces to the iron bath reactor 1' through line 30 92.5 tonnes of coal per hour, and through line 31 18.4 tonnes of additives or fluxes as slag generators per hour. Oxygen and water vapor, the gasification agents are injected through lines 32 and 33. Liquid slag, as the liquid reactor production of iron bath reactor 1', is withdrawn through slag output 34 in an amount of 29.4 t/h.

The gas obtained from the process in reactor 1' is fed via a 35 to a stage 36 for conversion of carbon monoxide, to adjust the necessary molar ratio of hydrogen to carbon monoxide. By injection of water through line 37 into the gas at about 1400°C, one obtains cooling of the gas obtained in the process, as well as conversion (cooling/conversion) of carbon monoxide present in the gas obtained in the process. The gas obtained in the process is thus enriched in hydrogen, so that a synthesis gas having a molar ratio of 2 mol hydrogen per 1 mol carbon monoxide is obtained. This synthesis gas, however, on leaving stage 36 for carbon monoxide conversion, contains CO₂ and is fed through gas line 38 to a stage 39 for separation of CO₂, which has an absorption column 40 and a desorption column 42.

The CO₂ can be removed from the synthesis gas by applying different known processes, for example, physicochemical absorption or washing with an NaOH solution.

In an advantageous form of the invention, in step 39 for separation of the CO₂, one provides for washing with hot potassium carbonate with divided flow. One therefore exploits the fact that during reaction of CO₂ with potassium carbonate in the aqueous phase, the curve obtained at equilibrium still presents a favorable course for absorption, even at elevated temperatures. Since absorption and desorption are carried out at temperatures very close to each other, it is not necessary to resort to cumbersome heat exchangers for the washing agent, which would otherwise be necessary. Another advantage consists of the fact that the absorbed acid component still retains a noticeable pressure up to limited loads, so that relatively little water vapor is necessary for hot regeneration.

In the CO₂ absorption stage 39, the synthesis gas-containing CO₂ is introduced under pressure of 3 bar at a temperature of 150°C to absorption column 40, in which extraction occurs by washing of the CO₂ by a chemical reaction:



The purified synthesis gas leaves the absorption column 40 through line 41 at about 50°C and is fed directly to methanol synthesis. The washing liquid loaded with CO₂ is fed to a recycling line to desorption column 42, at the input to which this washing liquid is expanded from 3 bar to atmospheric pressure. Evaporation of the water to achieve the corresponding saturation pressure is produced.

Within desorption column 42, washing liquid (KHCO₃ solution) is heated to 100°C with liberation of CO₂. The liberated CO₂ is withdrawn in the form of a CO₂/water vapor mixture through line 43 of the desorption column 42.

Heating of the desorption column 42 is carried out partly by the heat energy contained in the synthesis gas and the heat of the hot vapor introduced through line 44 and withdrawn again through line 45. Before being sent again to absorption column 40, the wash liquid is cooled to 40°C. For this purpose, the cooling water is introduced through line 46 into desorption column 42, which is withdrawn again after the cooling process through line 47.

Another operating method, as shown with the dashed line in Figure 2, can have the following aspect:

Conversion of carbon monoxide is only carried out on a gas stream 50, representing part of the gas obtained in iron bath reactor 1'. The other partial stream 51 of produced gas is sent to a cooling vessel 52, in which the heat energy of this partial stream of gas 51 permits production of steam. For this purpose, for example, one can introduce part of the cooling water, which was preheated by use, or even the condensate of the heating steam coming from the desorption column to cooling vessel 52 to produce steam. The steam can be fed partly as gasification agent to iron bath reactor 1' or, on the other hand, serve to heat the desorption column.

The CO₂/water vapor mixture liberated in desorption column 42, for example, can also be fed as gasification agent to iron bath reactor 1'. These measures permit an increase in the overall efficiency or overall yield of the process, or even the profitability of methanol synthesis.

In addition, at all necessary sites of the lines in the installation, one can position pressure measurement and regulation devices, devices to measure temperature and flow rate, as well as analysis equipment to determine the gas composition (for example, the CO and H₂ concentration).

TABLE 1

Line	Agent in mol/s	MW	T, K	P, bar	
30	Coal	92,5 t/h	-65,3	298	-
31	Flux (CaO)	18,4 t/h	-58,3	298	-
32	O ₂	794	0	298	3
33	H ₂ O	53 t/h	-12,7	400	3
34	Slag (CaS)	29,4 t/h	-78,7	1673	-
35	CO : 1664, H ₂	1049	-57,6	1673	3
37	H ₂ O	1673	-478,8	298	3
38	CO : 904, H ₂	1808	-536,4	840	3
and	CO : 760, H ₂ O	913	"	"	"
41	CO : 904, H ₂	1808	132,2	323	2,5
and	H ₂ O	142	"	"	"
43	CO ₂ : 760, H ₂ O	771	482,2	357	1,1
44	H ₂ O	690	161,9	523	5
45	H ₂ O	690	185,6	357	5
46	H ₂ O	38583	-11029	298	1
47	H ₂ O	38583	10927	333	1

CLAIMS

1. Process for preparation of a synthesis gas, consisting of hydrogen and carbon monoxide, characterized by the fact that gas without sulfur, obtained in an iron bath reactor by gasification of carbon-containing materials, especially coal, is enriched with additional hydrogen, so that this gas as synthesis gas has a molar ratio of 2 mol hydrogen per 1 mol carbon monoxide.

2. Process according to Claim 1, characterized by the fact that synthesis gas having a molar ratio of 2 mol hydrogen per 1 mol carbon monoxide is used as raw material for methanol synthesis.

3. Process according to Claim 1 or 2, characterized by the fact that the gas coming from the iron bath reactor is passed through a cooling vessel and then enriched with additional hydrogen.

4. Process according to any of the Claims 1 to 3, characterized by the fact that the additional hydrogen, intended to enrich the gas obtained in the iron bath reactor, is produced by electrolysis of water vapor at elevated temperature.

5. Process according to any of the Claims 1 to 4, characterized by the fact that decomposition of the water vapor is carried out by electrolysis at elevated temperature, preferably operating under a pressure of 35 bar and a temperature of 800°C, which causes decomposition of the water vapor to hydrogen and oxygen.

6. Process according to one of the Claims 4 and 5, characterized by the fact that the water vapor necessary for electrolysis at elevated temperature is produced in the cooling vessel.

7. Process according to any of the preceding claims, characterized by the fact that the hydrogen and oxygen produced by electrolysis at elevate temperature is passed through the cooling vessel.

8. Process according to any of the preceding claims, characterized by the fact that part of the oxygen produced by electrolysis at elevated temperatures is sent to the iron bath reactor.

9. Process according to any of the preceding claims, characterized by the fact that water vapor under pressure, which is preferably 3 bar, is produced in the cooling vessel and sent to the iron bath reactor.

10. Process according to one of the Claims 1 or 2, characterized by the fact that part of the gas obtained in the iron bath reactor is fed to a carbon monoxide conversion stage and a CO₂ absorption stage.

11. Process according to any of the preceding claims, characterized by the fact that, by conversion of carbon monoxide to hydrogen and CO₂, the additional hydrogen intended to enrich the gas produced in the iron gas reactor is obtained.

12. Process according to any of the preceding claims, characterized by the fact that conversion of carbon monoxide is carried out by injection of water into the gas coming from the iron bath reactor, and which is advantageously at 1400°C.

13. Process according to any of the preceding claims, characterized by the fact that the CO₂ is eliminated from the synthesis gas by absorption with hot potassium carbonate.

14. Apparatus for employment of the process according to any of the Claims 1 to 13, characterized by the fact that it contains an iron bath reactor (1) that is connected by gas lines (7, 11, 12, 15, 16, 18, 19) and a cooling vessel (2) to the hydrogen production apparatus (3, 36).

15. Apparatus according to Claim 14, characterized by the fact that the hydrogen production apparatus consists of a cell (3) for electrolysis at elevated temperature.

16. Apparatus according to Claim 14, characterized by the fact that the hydrogen production apparatus consists of a stage (36) for conversion of carbon monoxide, followed by a stage (39) for absorption of carbon monoxide.